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A mini review: Metal remediation by microbes and plants

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Abstract

Heavy metals are found naturally in the earth. In very small amounts, many of these metals are necessary to support life. However, in larger amounts, they become toxic. The microorganisms may be indigenous to a contaminated area or they may be isolated from elsewhere and brought to thecontaminated site. Binding of metal elements to bacterial surface is due to the anionic properties of the bacterial envelope that is able to absorb metal cations. Phytoremediation is the name given to a set of technologies that use different plants as a containment, destruction, or an extraction technique. Phytoremediation efforts have largely focused on the use of plants to accelerate degradation of organic contaminants, usually in concert with root rhizosphere microorganisms, or remove hazardous heavy metals from soils or water. Phytoremediation consists of different plant-based technologies such as rhizofiltration, phytoextraction, phytodegradation, phytostabilization, phytovolatization, and phytorestoration.

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Introduction

Heavy metals are found naturally in the earth. The heavy metals constitute a group of about 40 elements with a density greater than five (80). Even though many of them are essential for growth, They are main culprits polluting the environment and are caused by a number of human activities, such as mining, smelting, electroplating, use of pesticides, sludge dumping, and (phosphate) fertilizers as well as biosolids in agriculture (Ali *et al.*, 2013). In very small amounts, many of these metals are necessary to support life. However, in larger amounts, they become toxic. Because of its toxicity, metal contamination of the environment is also a serious problem. Recent study has been designed to provide quick access to information on the various bioremediation processes.

Microbial bioremediation

The microorganisms may be indigenous to a contami nated area or they may be isolated from elsewhere an d brought to thecontaminated site.Contaminant comp oundsare transformed by living organisms through re actions that take place as a part of their metabolic pro cesses. Microbial bioremediation has been somewhat successful for the degradation of certain organic contaminants, but is ineffective at addressing the challenge of toxic metal contamination, particularly in soil. For example *Bacillus polymyxa* utilize for remediation of Cu, *Pseudomonas*

Aeruginosa for Zn (Philip *et al.*, 2000; Gunasekaran *et al.*, 2003), *Zooglea* spp for U, Cu, Ni (Sar *et al.*, 1999; Sar and D'Souza, 2001), *Citrobacter* spp. for Co, Ni, Cd (Sar *et al.*, 1999; Sar and D'Souza, 2001), *Chlorella vulgar is* for Au, Cu, Ni, U, Pb (Yan and Viraraghavan, 2001; Gunasekaran *et al.*, 2003), *Aspergilus niger* for Cd, Zn Zn, Ag, Th (Pearson, 1969), *Rhizopus arrhizus* for Ag, Hg, P (Gunasekaran *et al.*, 2003).

Binding of metal elements to bacterial surface is due to the anionic properties of the bacterial envelope that is able to absorb metal cations (Sandaa *et al.*, 1999).There is two reasons that bacteria absorb metals: 1- Reduce the concentration of toxic metals in the environment and thus reduce its toxicity to bacteria 2- Storage the metal for the synthesis of their structural materials (Ehrlich, 1967).

In general, metals are divided into three categories in terms of availability and toxicity for bacteria. 1- Metals are frequently available for microorganisms and in normal concentrations (10-20 grams per liter) are not toxic, such as iron, calcium, magnesium.2- The metals, are relatively available for microorganisms and they are toxic. Microorganisms would not tolerate them usually higher than 1,000 ppm like silver, cadmium, and antimony. 3- The metals are toxic such as previous group but most of them are not actually available to microorganisms because of scarcity or insoluble compounds such as tungsten and many radioactive metals. Mechanisms of the metal binding to the cell wall include: electrostatic interaction: negative charge group (carboxyl, hydroxyl and phosphoryl) in bacterial cell wall attracts the positive charges in metals (Sandaa *et al.*, 1999). Physical adsorption or absorption of van der Waals: In this type of connection, the metal molecules are adsorbed parallel to the surface. The metal molecules are moving, but they cannot be far away from the outer surface of the cell. Chemical adsorption: anionic agents in the cell wall, are chemically reacts with the metal cations and a stable compound is formed (Sandaa *et al.*, 1999).

The unique property of elemental mercury is that it is a liquid at room temperature and thus is easily volatilized. Some bacteria, covert mercury into methylmercury -a volatile compound - and then transferred it to the external environment. This combination is removed from the environment as a gas.

However, because of its high reactivity, mercury in the environment exists mainly as a divalent cation Hg^{2+}. Bacteria can catalyze the reduction of the mercuric ion to elemental mercury using mercury reductase, a soluble NADPH-dependent FAD-containing disulfide oxidoreductase (NADPH, reduced nicotinamide adenine dinucleotide phosphate; FAD, flavin adenine dinucleotide) (Fox *et al.*, 1982).

Thiobacillus are capable of producing silver sulfide and then store it in their wall. So that the dry wall of these bacteria contains up to 25% of the sulfur silver. Some bacteria uptake iron from outside environment and convert it to trivalent iron or trivalent iron hydroxide inside cells. Thus, some toxic metal ions precipitate with trivalent iron hydroxide and toxic metal removed from the environment (Lombi, 2001). Therefore, today the use of microorganisms to clean up the environment, from heavy metals is durable and economic solution.

Phytoremediation

Pathway of metal/nutrient uptake in plants

Soluble metals can enter into the root symplast by crossing the plasma membrane of the root endodermal cells or they can enter the root apoplast through the space between cells. If the metal is translocated to aerial tissues, then it must enter the xylem. To enter the xylem, solutes must cross the Casparian strip, a waxy coating which is impermeable to solutes, unless they pass through the cells of the endodermis probably through the action of a membrane pump or channel. Once loaded into the xylem, the flow of the xylem sap will transport the metal to the leaves, where it must be loaded into the cells of the leaf, again crossing a membrane. Once in the shoot or leaf tissues, metals can be stored in various cell types, depending on the species and the form of the metal, since it can be converted into less toxic forms (to the plant) through chemical conversion or complexation. The metal can be sequestered in several subcellular compartments (cell wall, cytosol, and vacuole) or volatilized through the stomata.

Phytoremediation is the name given to a set of technologies that use different plants as a containment, destruction, or an extraction technique. Phytoremediation efforts have largely focused on the use of plants to accelerate degradation of organic contaminants, usually in concert with root rhizosphere microorganisms, or remove hazardous heavy metals from soils or water. Phytoremediation has recently become a subject of intense public and scientific interest and a topic of many recent reviews.

Nonradioactive As, Cd, Cu, Hg, Pb and Zn and radioactive Sr, Cs and U (referred to here as toxic metals) are the most environmentally important metallic pollutants. Phytoremediation consists of different plant-based technologies such as rhizofiltration, phytoextraction, phytodegradation, phytostabilization, phytovolatization, and phytorestoration (McGrath, 2003).

Rhizofiltration: Rhizofiltration is a type of phytoremediation, which refers to the approach of using hydroponically cultivated plant roots to remediate contaminated water through absorption, concentration, and precipitation of pollutants. Many plant species naturally uptake heavy metals and excessnutrients. Both phytoextraction and rhizofiltration follow the same basic path to remediation. First, plants are put in contact with the contamination. They absorb contaminants through their root systems and store them in root biomass and/or transport them up into the stems and/or leaves. The plants continue to absorb contaminants until they are harvested. Both processes are also aimed more toward concentrating and precipitating heavy metals than organic contaminants. The major difference between rhizofiltration and phytoextraction is that rhizofiltration is used for treatment in aquatic environments, while phytoextraction deals with soil remediation (Dushenkov *et al.*, 1995).

Phytoextraction: Phytoextraction involves the removal of toxins, especially heavy metals and metalloids, by the roots of the plants with subsequent transport to aerial plant organs (Salt *et al.* 1998;

Lombi *et al.* 2001). Pollutants accumulated in stems and leaves are harvested with accumulating plants and removed from the site. In the case of heavy metals, chelators like EDTA assist in mobilization and subsequent accumulation of soil contaminants such as lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn) in *Brassica juncea* (Indian mustard) and *Helianthus anuus* (sunflower) (Blaylock *et al.* 1997; Turgut *et al.* 2004). Most of the work on the mechanisms of root and plant cell uptake has focused on the study of N, P, S, Fe, Ca, K and possibly Cl (Marschner *et al.*, 1995). However, little is known about the mechanisms of mobilization, uptake and transport of most environmentally hazardous heavy metals. Metal-chelating molecules can be secreted into the rhizosphere to chelate and solubilize 'soil-bound' metal. Until now, the major successes in phytoextraction were achieved by applying synthetic chelates to the soil (Robinson, 1993).Roots can reduce 'soil-bound' metal ions by specific plasma membrane bound metal reductases, which may increase metal availability (Kramer *et al.*, 1996). Plant roots can solubilize soil-bound toxic metals by acidifying their soil environment with protons extruded from the roots (Crowley *et al.*, 1991). Roots can employ rhizospheric organisms (mycorrhizal fungi or root-colonizing bacteria) to increase the bioavailability of metals. Mobilized metals are taken up by plant roots from the soil solution and exported to the shoots (Guerinot *et al.*, 1994).

Phytostabilization: phytostabilization focuses mainly on sequestering pollutants in soil near the roots but not in plant tissues (Rubin, 2001). Phytostabilization involves the use of plants to limit the mobility and bioavailability of metals in soil.

Phytovolatization: Toxic metals such as Se, as and Hg can be biomethylated to form volatile molecules that can be lost to the atmosphere (Bauelos *et al.*, 1990). The advantage of this method is that the contaminant, mercuric ion, may be transformed into a less toxic substance. The disadvantage to this is that the mercury released into the atmosphere is likely to be recycled by precipitation and then redeposited back into lakes and oceans, repeating the production of methyl-mercury by anaerobic bacteria (Ruiz, 2003).

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